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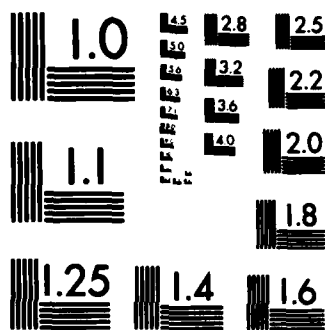
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"ELEMENTARY REACTIONS OF IMPORTANCE IN OXIDATION, COMBUSTION
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FINAL REPORT

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PRINCIPAL INVESTIGATOR: DR. SIDNEY W. BENSON

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FINAL REPORT

The last three years have been very eventful and fruitful in terms of scientific achievement and publication. After an initial rebuilding period in 1976-1977 during which our laboratory was moved from SRI and reestablished at USC we began a program under ARO sponsorship of investigating the chemistry and mechanisms associated with cool flames, ignition, combustion and inhibition. We can now testify to impressive progress in all of these areas as well as significant new results in related areas. Our investigations have included both experimental and theoretical studies and these are summarized briefly here.

I. Mechanism in Combustion and Related Processes

We have now completed for the first time a molecular mechanism which includes rate constants for all the key steps in the oxidation and combustion of CH_4 to C_3H_8 hydrocarbons (363,382). We can account for cool flames, the induction periods leading to cool flames, the hot ignition or quenching following cool flames and the induction periods leading to hot ignition. The same mechanism successfully account for the oxidation and breakdown of lubricating oils and for the periodic flames observed in oxidizing flow systems. This work can now offer a framework within dynamic effects may be investigated. We have also elucidated the mechanisms of oxidation of HI (371), HCl and HBr (372) and the formation of soot in hydrocarbon flames.

II. Thermochemistry of Radicals Important in Combustion Process

In order to provide the detailed mechanism of oxidation we have had to

measure thermochemical properties (ΔH_f° , S° and C_p°) of some key radicals. These include the following: HO_2 (378,381), CH_3O_2 (391), tBuO_2 (377), EtOCHCH_3 (385), tBu (386), CH_3CO (387) and CHCl_2 (369). Sulfur has turned out to be a very important species in combustion, primarily because of its contribution to air pollution and acid rain. These in turn will have impacts on the kinds of fuels we will use in the future and/or the kinds of emission controls that may be required on combustion devices. This has inspired us to investigate the chemistry of organic sulfur containing radicals and the mechanisms of their pyrolysis and oxidation. In the course of this work we have measured thermochemical properties for $\text{CH}_3\text{S}^\cdot$ (373), CH_2SCH_3 (393) and a number of related molecular and radical species. From this have come new insights into mechanisms of isomerization and pyrolysis of sulfur containing agencies (394) and the first insight into COS and CS_2 formation in flames and incinerators.

III. Theoretical Studies in Kinetics

Perhaps one of our most important studies has been those on recombination and disproportionation of alkyl radicals (375). This establishes a model which can reproduce the respective rate constants to within 20% over the temperature range from ambient to flame temperatures. This has as one immediate consequence the ability to predict the inverse rate constants for bond fission and molecule/olefin disproportionation just from knowledge of molecular structure.

Another important achievement has been to construct a model which has been able to explain the very puzzling negative activation energies observed in low temperature atmospheric processes (388). Rate constants at 200-350°K have frequently been very different from their values extrapolated from observations in flame systems at 1600-2200°K. Our new

model now explains these anomalies for the very important flame reaction $\text{OH} + \text{CO}$ (389) for HO_2 self-reactions (392) and for OH reactions with polar species (390).

A very important observation known for some time from (TST) transition state theory but now confirmed in flame studies is that the 2-parameter Arrhenius equation is inadequate to represent rate constants over any large temperature require. One needs to use the 3-parameter form $AT^m \exp(-E/RT)$ and it can be shown that m can be calculated from TST with much better precision than it can be measured.

IV. Experimental Design

One of our most useful employments in this recent period has been the redesign of our VLPR system to use turbo-molecular pumps and additional pumping stages. It is now close in operation to a molecular beam system and can measure atoms down to $10^9/\text{cc}$ and radicals down to $10^{10}/\text{cc}$. We are still studying the sensitivity and performance of the system in detail. Recently we found that our microwave discharge produced both ground and excited state of halogen atoms. This has been of importance only with Br where the discovery has made possible the measurement of rate constant of $\text{Br}(^2P_{1/2})$ as well as ground state ($^2P_{3/2}$). This is a continuing process limited only by available funds and manpower.

To avoid excited electronic states we have explored and developed thermal sources for Br and Cl atoms which seem to work well.

V. Theory of Ionic Solvation

Convinced that ion-pairs and ionic processes may play a role in low temperature oxidations we have begun theoretical studies of potential functions to describe ion-ion and ion-solvent interactions

(361,362,379,380). These have been very successful in accounting for ΔH_f° diatomic alkali halide molecule, crystals and dimers as well as successive hydration energies of individual ions.

SCIENTIFIC PERSONNEL SHOWING ADVANCED DEGREES EARNED BY THEM WHILE EMPLOYED ON THE PROJECT:

1. Lilian Shum - graduate student received Ph.D
2. Shawn P. Heneghan - graduate student received Ph.D
3. Kenneth Kosnik - graduate student received Ph.D
4. Maia Vaisman - graduate student received Ph.D

POST-DOCTORATES AND VISITING FACULTY

1. Professor Roger Marshall
2. Professor B. Thimme Gowda
3. Professor Tajmeri Islam
4. Dr. Michael Mozurkovich
5. Dr. John J. Lamb

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